Synthesis & Characterization of mixed metal MOF for Supercapacitor application

Synopsis in candidature for the degree of

Doctor of philosophy in physics

Submitted By

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1.1 Introduction

Now a day's an enormous interest in the growth of energy storage devices with both high energy density and high power density, with supercapacitors being one of the most favorable candidates, as they typically have higher power densities and longer cycling lives than batteries [1]. Thus, research efforts on supercapacitors are focused on achieving higher energy densities, and the development of new materials is of paramount importance to achieve this goal [2, 3].

Throughout the progress of supercapacitor, porous materials, which are able to enable fast mass and electron transportation for energy storage, have always been a research hotspot [4]. Yaghi et al. well-defined a new class of porous material in 1990, i.e., metal-organic frameworks (MOFs). MOFs are well recognized for their porous crystalline architectures with periodic networks comprised of rich metal centers. This new member of crystalline materials in which organic ligands are repeatedly coordinated to metal cations, have triggered numerous interests and gradually being considered as one of the best links between the fields of nanotechnology and energy storage due to their essential advantages, including abundant pores, high specific surface area, morphology, and multifunctionalities [5-8]. By varying the coordinating sites and size of linkers in MOFs, the size and volume of their pores can be tuned easily.

As per current research scenario, MOFs and their derived nanostructures have been widely renowned for their great application possibilities in solar cells, electrochemical sensors, fuel cells, supercapacitors, and Li-ion batteries [9-10]. Mixed metallic metal-organic frameworks (M-MOFs) are advanced materials with enhanced framework complexity to achieve improved performances compared to single metal MOFs [11]. M-MOFs consist of two or more different metal nodes in the MOF unit. It is also possible to have immobilized metal ions, metal complex/nanoparticles and organometallic units anywhere in the MOF unit with or without interactions and their structure delivers attractive multi-functionality/ complexity and tunable properties for specific applications [12-13].

1.2 Literature review

Recently, M-MOFs have attracted great attention in supercapacitor applications [14-15]. Afterwards, the development of electrochemically active M-MOFs for direct usage in supercapacitors is one of the important tasks. Some reports have presented the direct use of M-MOFs for supercapacitor application [16]. Ranjbar's [17] group first reported a bimetallic MOF for supercapacitor application. The Ni/Co-MOF was prepared via the direct synthesis approach and

the resultant M-MOF exhibited a 3D framework. The structural analysis suggested that the Ni^{2+} and Co^{2+} metal ions were equally distributed in the Ni/Co- MOF framework, where the occupation of each metal ion was 50%, which was also verified by the ICP technique. The MOF revealed outstanding stability and retained 97.4% of its original capacitance after 5000 cycles, signifying its capacity as a favorable Pseudocapacitive material. The solvothermal method is used by Xi et al. to prepare hallow structured Ni-MOF and Ni/Co-MOF nanoflakes, which exhibit excellent supercapacitor electrode [18]. However, M-MOFs and their derived materials have not been fully explored to date, and the number of reported synthetic routes is limited. To the best of our knowledge, there have been very few studies on the application of these M-MOFs in Supercapacitor. Therefore, we will have synthesized Ni-MOF, Co-MOF, Ni/Co-MOF, Fe/Co-MOF electrodes using one of the appropriate chemical methods for supercapacitor device fabrication.

1.3 Aim

The first aim of this work is to synthesis of different M-MOF. Second is to use the M-MOF for supercapacitor device fabrication using two electrode system. The ultimate aim of this work is to enhance the energy density, power density, rate of cycle life in supercapacitor.

1.4 Objectives:

The main objective of this synopsis to develop and synthesis M-MOF's for high performance supercapacitor device fabrication.

- Synthesis of M-MOF electrodes such as Ni-MOF, Co-MOF, Ni/Co-MOF, Fe/Co-MOF nanostructure using appropriate chemical synthesis methods.
- Structural and morphological properties of the prepared nanostructured electrodes will be studied using various characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, etc.
- Electrochemical performance will be studied in various electrolyte solutions with different molarity.
- Rate capability and capacitance retention will be studied.
- Symmetric/asymmetric device will be fabricated.

1.5 Methodology:

There are few chemical methods are used for synthesis of M-MOF electrodes such as hydrothermal deposition (HD), solvothermal method, slow diffusion technique, etc. Among these methods, optimized method will be used for synthesis of M-MOF's electrodes for supercapacitor application.

Hydrothermal method;

Many types of nanomaterial/metal oxide have been successfully synthesized by using hydrothermal. There are significant advantages of hydrothermal synthesis method over others. Hydrothermal synthesis can generate nanomaterial which are not stable at elevated temperatures. Nanomaterial with high vapor pressures can be produced by the hydrothermal method with minimum loss of materials. The compositions of nanomaterial to be synthesized can be well controlled in hydrothermal synthesis through liquid phase or multiphase chemical reactions.

Solvothermal Method;

Solvothermal synthesis is defined as a chemical reaction that takes place in a solvent at a temperature higher than the boiling temperature of the solvent in a sealed vessel. This method provides precise control over the particle size and shape distribution by adjusting the reaction parameters.

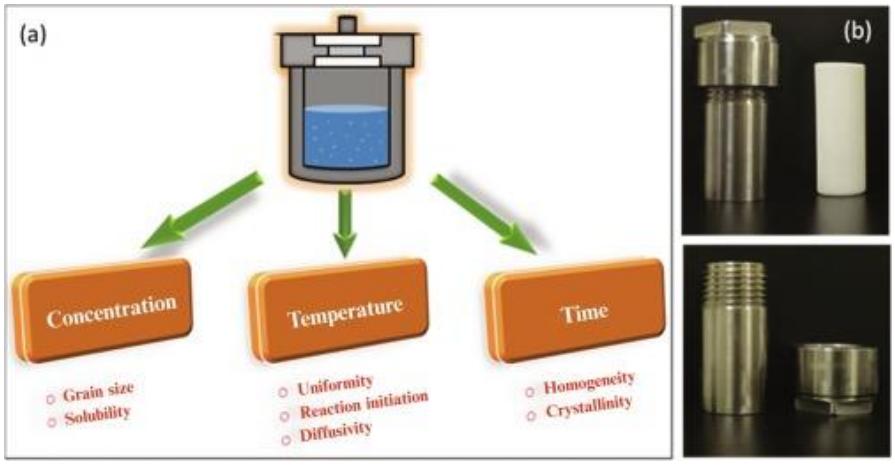

Fig.1. Schematic of autoclave used in the solvothermal process and (B) the photograph of steel chamber and Teflon liner used to contain a solution.

Other methods will be adopted if necessary.

1.6 Experimental section

Synthesized M-MOF's electrodes will be characterized by using different analytical tools and techniques such as X-ray diffraction (XRD), Raman spectroscopy, Fourier Transform Infrared Spectroscopy, Field Emission Scanning Electron Microscopy (FE-SEM), High Resolution Transmission Electron Microscopy (HR-TEM) X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), etc.

Electrochemical workstation will be used to study the electrochemical properties and device fabrication such as cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), stability, rate capability, and impedance spectroscopy, etc. Finally, carried work will be submitted to the university for the award of Ph.D. in the form of thesis.

1.7 Work plan

The proposed work will be carried out in following phases:

Phase – I (First Year)

- In the first year, literature survey will be carried out. The various M-MOF will be prepared using suitable synthesis method.

Phase – II (Second Year)

- The electrochemical performance of the prepared M-MOF will be measured and studied in different electrolyte such as KOH, H_2SO_4, NaOH, KCL, etc.

Phase – III (Third Year)

- To the study the industrial potential of the prepared M-MOF's, the symmetric /asymmetric device will be fabricated.
- The work will be communicated time to time with the high impact journals.

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